CHEMICAL ENGINEERING TRANSACTIONS Volume 17, 2009
Editor Sauro Pierucci
Copyright © 2009, AIDIC Servizi S.r.l., ISBN 978-88-95608-01-3 ISSN 1974-9791
DOI: 10.3303/CET0917004

Platinum catalysts for the low temperature catalytic steam reforming of ethanol

Paolo Ciambelli[a], Vincenzo. Palma[a*], Arianna Ruggiero[a], Gaetano. Iaquaniello[b]
[a]Dipartimento di Ingegneria Chimica e Alimentare, Università degli Studi di Salerno,
Via Ponte Don Melillo, 84084 Fisciano (SA), Italy
[b]Technip KTI S.p.A., Viale Castello della Magliana 75, 00184 Roma, Italy
[*]Corresponding author. E-mail address: vpalma@unisa.it

Electric power generation by H_2 fuel cells is the most promising technology for the reduction of fossil fuels dependence, greenhouse gas emissions and atmospheric pollution. Among different H_2 sources ethanol is very attractive when obtained from biomass minimizing CO_2 emissions. At low temperature ethanol steam reforming to H_2 or pre-reforming to CH_4 can increase the overall system efficiency, but the by-products formation leads to reduced selectivity and catalyst durability because of coke formation. The feasibility of this process is strictly correlated to both technological and economical aspects. In this work the performance of Pt based catalysts supported on Al_2O_3 and CeO_2 has been studied and compared in terms of catalytic activity and selectivity in the temperature range 300-450 °C. Moreover the techno-economic feasibility of green energy production via steam reforming of bio-ethanol (ESR) was evaluated.

1. Introduction

In the last years H_2 attracts significant research interest because it is a clean fuel without co-production of greenhouse gases. Commercially, hydrogen has been produced from catalytic steam reforming of fossil fuels as methane “Rostrup-Nielsen (1984)”. To reduce the greenhouse gas emissions, H_2 should be derived from renewable fuels such as bioethanol “Huber et al. (2003), Cortright et al. (2002), Deluga et al. (2004)”. As a consequence, ESR has been studied, as it provides an alternative fuel source for hydrogen production. In ESR to produce H_2 for PEM fuel cells, high-reforming temperatures also favor CO formation, which poisons the anode. As a result, CO reduction processes are required. The high-reforming temperature coupled with the lower temperature water gas shift step suffers from thermal inefficiencies. Low temperatures ESR allows high system efficiency and lower hardware construction costs. However, at low temperatures, CH_4 and undesirable byproducts(coke precursors) are thermodynamically favored “Garcia and Laborde (1991), Vasudeva et al. (1996), Fishtik at al. (2000), Mas et al. (2006)”, reducing H_2 selectivity and catalyst life. Thus, kinetic rather than thermodynamic control of the reaction is required. Moreover high ethanol conversion is vital for the process economy. On the other hand, since at low temperature CH_4 is thermodynamically favoured, a process strategy is the integration of H_2 production by steam reforming with CH_4 production by pre-reforming; CH_4 could be

Please cite this article as: Ciambelli P., Palma V., Ruggiero A. and Iaquaniello G., (2009), Platinum catalysts for the low temperature catalytic steam reforming of ethanol, Chemical Engineering Transactions, 17, 19-24 DOI: 10.3303/CET0917004

converted to H_2 in a following steam reforming stage. The feasibility of this process is strictly correlated to both technological and economical aspects. The development of an high performance catalyst able to assure the production of H_2 and CH_4 rich stream by low temperature steam reforming of bio-ethanol, as well as the costs comparison of bio-ethanol steam reforming (ESR) with the conventional steam methane reforming (SMR) process are essential requirements to asses the suitability of the former for clean and renewable energy production.

The objective of the present study therefore was to develop a new, highly efficient and cost effective process for green energy production by ethanol steam reforming at low temperature. Therefore the performance in ESR of Pt based catalysts has been studied by varying support (Al_2O_3 and CeO_2), metal loading and temperature (300-450 °C). Moreover, the techno-economic feasibility of ESR for energy production was evaluated.

2. Experimental

2.1 Catalyst preparation

Commercially available CeO_2 (Aldrich) and Al_2O_3 (Fisons) with a BET surface area of 80 and 160 m^2/g, respectively, were used as support. Pt-containing catalysts were prepared by impregnating the support with aqueous solution of $PtCl_4$, drying at 120 °C overnight and calcining for 3h in air at 600 °C (dT/dt=10°C/min).

2.2 Catalytic activity testing

Ethanol steam reforming laboratory plant was sketched in Figure 1

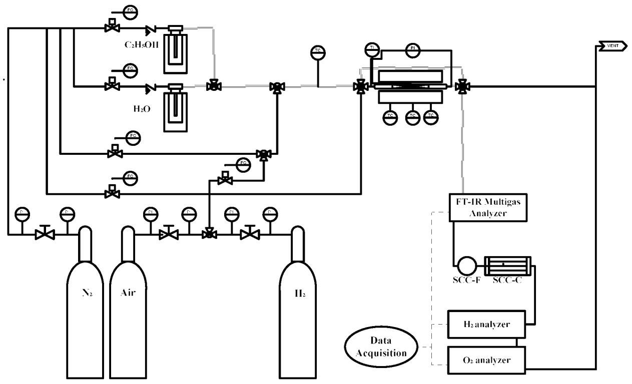

Figure 1 Ethanol steam reforming laboratory plant.

Catalytic activity tests were performed on powder catalyst (180 ÷ 355 μm) in the range 300 ÷ 450°C in a continuous flow fixed bed reactor (18 mm i.d) placed in a three zone electric oven, at atmospheric pressure. Ethanol and water were fed by saturating an N_2 flow at fixed temperature. The mixture was diluted with a N_2 stream, giving a typical feed gas composition of $C_2H_5OH/H_2O/N_2 = 0.5/1.5/98$ vol %. The GHSV was 15000 h^{-1} and the reactor outlet concentrations of C_2H_5OH, H_2O, CH_4, CO, CO_2 and other by-products were monitored with an on line Nicolet Antaris IGS FT-IR multigas analyzer, equipped with an heated gas cell operating at temperatures up to 185 °C and an MCT-A N_2 liquid cooled detector. The dedicated analysis software is able to follow up to 100 different gaseous species simultaneously. The data were acquired at 0.5 cm^{-1}, and cell temperature and pressure were monitored and used to correct gas concentrations. The H_2 and O_2 concentrations in the gas stream were measured respectively by CALDOS 27 and MAGNOS 206, ABB analyzers.

3. Results

3.1 Effect of support and metal loading

The role of the support and metal loading in ethanol steam reforming reaction was examined using Pt as the active metal whose loading was varied from 1 to 3 wt %. Also a commercial catalyst 0.3-Pt/al_2O_3 Engelhard was tested.

The supports have no activity in ethanol steam reforming reaction as appeared from the test carried out at 300 °C (not reported). Ethanol conversion and hydrogen yield as function of time on stream for Pt based catalysts tested are reported in Figure 2.

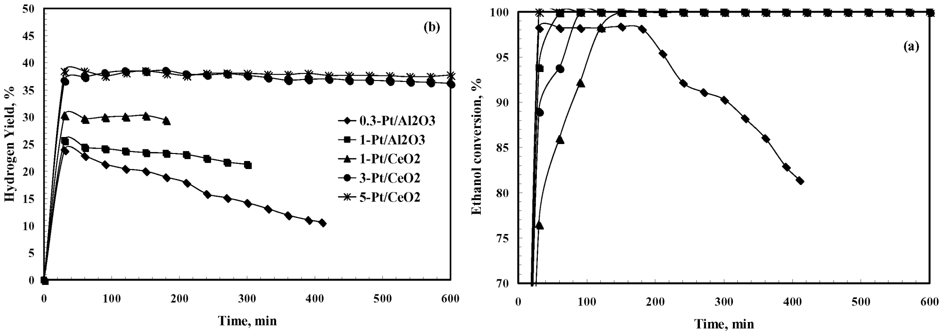

Figure 2 Ethanol conversion (a) and hydrogen yield (b) in ESR on CeO_2 and Al_2O_3 supported Pt catalysts with different metal loading versus time on stream. Experimental conditions: T = 300 °C, EtOH = 0.5 vol%, $EtOH:H_2O:N_2$ = 0.5:1.5:98, Total gas flow rate= 1000 (stp)cm^3/min, GHSV = 15000 h^{-1}.

For Pt/CeO_2 catalysts a transient time is observed in the ethanol conversion behaviour. Experimental results show that the time required to reach the apparent ethanol complete conversion decreases by increasing Pt loading, it disappears for the highest metal content. For the 1-Pt/Al_2O_3 sample it is observed a similar tendency of 1-Pt/CeO_2 catalytic system, even if a lower H_2 yield is observed. In the case of commercial catalyst 0.3-Pt/Al_2O_3 (Engelhard) the ethanol conversion is total only in the first three hours and decreases progressively until the end of the test. Hydrogen yield is higher and more stable for Pt/CeO_2 catalysts in respect to Pt/Al_2O_3 catalysts, moreover on both supports it increases with metal loading. In contrast with the conversion behavior, in the H_2 yield curves, no transient time is observed. Products distribution was strongly influenced from the nature of the support and the metal loading. In Table 1 is shown the selectivity of reaction products. H_2 and CO_2 selectivity are higher on Pt/CeO_2 catalysts; the samples with the higher metal content are the most selective to CO_2 and H_2 among the systems examined. CO selectivity is lower on Pt/CeO_2 catalysts; no formation of CO is detected on 5-Pt/CeO_2. Pt/Al_2O_3 catalysts are more selective to CH_4 and CO; CH_4 selectivity increases on Pt/CeO_2 by increasing metal content. The selectivity to H_2, CO and CO_2 are related via the water gas shift reaction, while the selectivity toward CH_4 is independent of that and is related only to the ethanol decomposition and steam reforming reactions. Based on product distribution results, the catalytic systems examined have not the same WGS activity, Pt/CeO_2 is much more active than Pt/Al_2O_3 catalyst. The activity in WGS reaction is enhanced by increasing metal loading.

Table 1 Products distribution in ESR on CeO_2 and Al_2O_3 supported Pt catalysts with different metal loading. Experimental conditions: T = 300 °C, EtOH = 0.5 vol%, EtOH:H_2O:N_2 = 0.5:1.5:98, Total gas flow rate= 1000 (stp)cm^3/min, GHSV = 15000 h-1, Time on stream = 3 h.

Catalyst	S_{CH4} (%)	S_{CO}(%)	S_{CO2}(%)	S_{H2} (%)	S_{C2H4} (%)	S_{C3H6O} (%)	S_C (%)
0.3-Pt/Al_2O_3	36.8	42.6	8.1	19.3	25.1	5.0	-
1-Pt/Al_2O_3	39.3	45.2	4.0	23.4	9	-	-
1-Pt/CeO_2	31.5	21.0	25.8	29.5	-	16.2	-
3-Pt/CeO_2	43.5	1.6	56.4	38.6	-	1.2	-
5-Pt/CeO_2	40.2	0	58.8	38.0	-	-	-
Equilibrium	56	0	33	18	0	0	10

Selectivity were calculated according to the following equations:

$$S_i = \frac{n_i/2}{n_{C2H5OH}^{in} - n_{C2H5OH}^{out}} \quad \textit{where i is } CO, CO_2 \textit{ and } C; \quad S_{H2} = \frac{n_{H2}/6}{n_{C2H5OH}^{in} - n_{C2H5OH}^{out}}; \quad S_{CH3CHO} = \frac{n_{CH3CHO}}{n_{C2H5OH}^{in} - n_{C2H5OH}^{out}}; \quad S_{C2H4} = \frac{n_{C2H4}}{n_{C2H5OH}^{in} - n_{C2H5OH}^{out}};$$

The main secondary products observed on the catalysts tested are ethylene on Pt/Al_2O_3 and acetone on Pt/CeO_2.

3.2 Effect of temperature

The effect of temperature was also investigated. The results, in terms of conversion, yield and selectivity as function of temperature, of 5-Pt/CeO_2 catalyst, are shown in Table 2.

Table 2 Effect of temperature on ethanol and water conversion, H_2 yield and products distribution in ESR on 5-Pt/CeO_2 catalyst. T = 300 °C, EtOH = 0.5 vol%, EtOH:H_2O:N_2 = 0.5:1.5:98; Gas flow rate = (stp)1000 cm^3/min, GHSV = 15000 h^{-1}, Time on stream = 3 h.

Temperature, °C	X_{EtOH} (%)	X_{H2O}(%)	Y_{H2}(%)	S_{CH4} (%)	S_{CO}(%)	S_{CO2}(%)	S_{H2} (%)
300	100	30.2	38	40.2	0	58.8	38.0
350	100	43.4	44.3	38.8	0	60.2	44.3
450	100	52.4	65.1	29.1	4.0	61.8	65.1

Ethanol conversion was always complete, while water conversion and H_2 yield increase from 300 to 450 °C. The overall H_2 production increase with temperature, but product distribution show that at higher temperature CH_4 selectivity decreases, and trace amounts of CO compare, due to the occurrence of CH_4 steam reforming reaction. For this reason, intermediate temperatures allows high H_2 and CH_4 production, and minimize CO formation.

4. Techno-economic evaluation

Figure 3 depicts a preliminary block diagram where the heat to convert the ethanol at low temperature is extracted from the sensible heat of the flue gases generated by reforming the methane left over. By such integration export steam can be minimised and the conventional reforming section becomes only a fraction of what required for an equivalent hydrogen production based on natural gas. In Table 3 some technical and economic features are compared together with the Capital Investment (ISBL) for the hybrid ESR+SR and conventional SR.

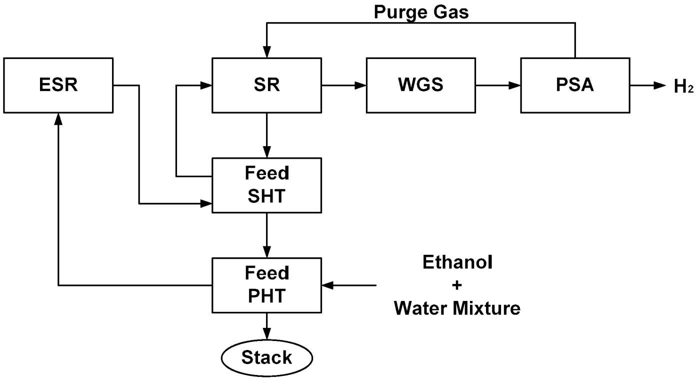

Figure 3 Block diagram of ESR-SR hybrid system

For the same hydrogen capacity the hybrid scheme should cost only 80 % of conventional SR, due to the reduction of the reforming section and elimination of desulphurisation section.

Table 3 Technical and economic data for SR and SR + ESR technology

Technology	SR	ESR + SR
Capacity, Nm^3/h H_2	1500	1500
Reforming section duty, Mkcal/h	1417	1205
Feed	620 Nm^3/h of Natural gas	784 kg/h of Ethanol
Capital investment, million of €	5,0	4,0 (1)

(1) based on reforming section with 85 % of a conventional one and elimination of the desulfurization section

In Table 4 a tentative production cost is calculated using for the variable cost only the cost of feed and for the fixed cost it has been assumed a working life of 15 years and a return on investment (WACC) of 9,5%.

Table 4 Production costs

Technology	SR	SR + ESR
Variable costs	0.062 (1)	0.073
Fixed costs	0.051 (2)	0.040
Éroduction costs, € perNm^3 H_2	0.113	0.113

(1) $\frac{620}{1500} \times 0.15$ € per Nm^3 H_2 ; (2) Capital Investment / (8400 x 1500 x 7.828); 7.828 = (annuity factor).

From such data the cost of the ethanol mixture which makes the production cost equal to natural gas based, has been calculated. At 0.14. Euro per kg of ethanol in a water ethanol mixture, the production makes an economic sense and becomes attractive.

A more advanced scheme is presented in Figure 4, where between the EPS reactor and the conventional methane reformer, a H_2 selective membrane module is inserted. In such a scheme H_2 produced in the pre-reformer step is recovered before entering the second reforming step, enhancing the CH_4 conversion, reducing the Capital Investment.

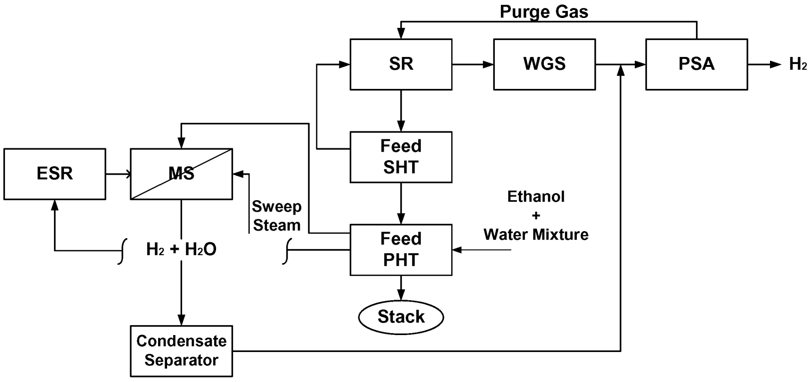

Figure 4 Block diagram of ESR-SR hybrid system with H_2 selective membrane separator

5. Conclusions

ESR test performed in the range 300-450 °C on different catalyst showed the relevance of the support and metal loading on the final performances in terms of activity, selectivity and durability. In particular, 5-Pt/CeO_2 sample allow a complete ethanol conversion without C formation in the whole temperature range. The economic feasibility of green energy production via steam reforming of bio-ethanol (ESR) was evaluated and two hybrid processes scheme were proposed where the H_2 production cost is only 80 % of conventional SR, due to the reduction of the reforming section and elimination of desulphurisation section.

References

Cortright R. D., Davda R.R., Dumesic J.A., 2002, Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water, Nature 418, 964-967.

Deluga G.A., Salge J.R., Schmidt L.D., Verykios X.E., 2004, Renewable hydrogen from ethanol by autothermal reforming, Science 303, 993-997.

Fishtik I., Alexander A., Datta R., Geana D., 2000, A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reaction, Int. J. Hydrogen Energy 25, 31-45.

Garcia E. Y., Laborde M. A., 1991, Hydrogen production by steam reforming of ethanol: thermodynamic analysis, Int. J. Hydrogen Energy 16 (5), 307-312.

Huber G.W., Shabaker J.W., Dumesic J.A., 2003, Raney Ni-Sn catalyst for H2 production from biomass-derived hydrocarbons, Science 300, 2075-2077.

Mas V., Kipreos R., Amadeo N., Laborde M., 2006, Thermodynamic analysis of ethanol/water system with the stoichiometric method, Int. J. Hydrogen Energy 31, 21-28.

Rostrup-Nielsen J.R., 1984, Catalysis Science and Technology, vol. 5, Eds. Anderson J. R. and Boudart M., Springer, Berlin.

Vasudeva K., Mitra N., Umasankar P., Dhingra S.C., 1996, Steam reforming of ethanol for hydrogen production: thermodynamic analysis, Int. J. Hydrogen Energy 21 (1), 13-18.